



(1) Publication number:

0 323 142 B1

(12)

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 08.09.93 (51) Int. Cl.5: C08L 71/00, C08L 79/08, C08L 83/06, H01B 3/30

(21) Application number: 88312187.3

2 Date of filing: 22.12.88

The file contains technical information submitted after the application was filed and not included in this specification

- (54) Ternary blends as wire insulations.
- Priority: 24.12.87 GB 8730130 20.04.88 GB 8809274
- 43 Date of publication of application: 05.07.89 Bulletin 89/27
- 45) Publication of the grant of the patent: 08.09.93 Bulletin 93/36
- Designated Contracting States: BE DE ES FR GB IT NL
- (6) References cited:

EP-A- 0 095 174 EP-A- 0 254 488 EP-A- 0 163 464

EP-A- 0 266 595

DE-A- 3 813 321

US-A- 4 250 279

- 73 Proprietor: PIRELLI GENERAL plc 40 Chancery Lane London WC2A 1JH(GB)
- Inventor: Alesbury, Colin Kevin 3 Forest Gate Mapley Southampton Hampshire S04 1GW(GB) Inventor: Murphy, Richard John, Dr. 26 Saker Street Liverpool(GB)
- (74) Representative: West, Alan Harry et al R.G.C. Jenkins & Co. 26 Caxton Street London SW1H 0RJ (GB)

Property of: Loctite Aerospace **R&D** Technical Library Return to library for filing when done.

> Copyright fees paid. Further copies require compliance with copyright restrictions.

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

and the polyether ketone ketone suitably contains repeating units of the general formula

in which in all cases (III) to (V) the phenylene groups may carry one or more substituents. The polyetherimide will generally contain repeating units of the general formula

in which Z and R are organic groups, for example in which R is

Z is

10

25

30

or a group of the formula

in which X is C_yH_{2y} ,

50

EP 0 323 142 B1

(as is the case with polyethylenes) after the addition of a sensitiser, for example triallyl isocyanurate (TAIC) and N,N-metaphenylene dimaleimide (such as that available as HVA-2 from Du Pont), by irradiation.

The blends according to the invention have excellent resistance to environmental stress crazing in halogenated solvents and aviation fuel, and exhibit improved flexibility and flame retardance compared to PEEK alone.

These properties, in conjunction with good abrasion resistance, low toxic fume emission and smoke evolution, little or no halogen content and a wide temperature range of operation enable the use of the blends in high performance electronic and electrical wiring applications such as aircraft, ship and vehicle electrical systems, mass transit systems and high temperature equipment, as a single layer insulation or as the inner and/or outer layer of a double layer insulation.

Blending may be carried out at an elevated temperature for example from 300 to 400 °C, for example in a twin screw mixer. A range of useful blends may be obtained in this manner containing from 5 to 95% by weight PEEK or PEK, from 5 to 95% by weight PEI and up to 80% by weight S-PI, based on the blend. However, when the blend is to be used as a single layer insulation, then the PEEK content of the blend is preferably at least 45% by weight.

As described below in greater detail, blends according to the invention have been tested according to Defence Standard 61-12 (Part 18) Issue 2 and it has been found that blends containing from 45 to 95% by weight PEEK and up to 54% by weight PEI/S-PI comply with that standard. A preferred composition in this respect contains, by weight, 60% PEEK, 5% PEI and 35% S-PI.

Suitable materials for use in the blends of the invention include the PEEK material available from ICI under the trade name "Victrex", the PEK material available from Hoechst Plastics under the trade name "Hostatec" and the PEI and S-PI materials available from General Electric Plastics and General Electric Silicones under the trade names "Ultem" and "Siltem", respectively.

By way of illustration of the invention, a number of PEEK/PEI/S-PI blends were prepared and each was coated onto a tinned copper conductor by extrusion. The resulting wires were tested and found to comply with Defence Standard 61-12 (Part 18) Issue 2, as follows:

TABLE 1

Critical (Oxygen Ind	ex (clause 8	3.2.7)
compo	osition (weig	oxygen index, %	
PEEK	PEI	S-PI	Specification limit, 29%
15	15	70	50
20	20	60	51
25	25	50	48
50	25	25	53
70	15	15	41

45

40

20

30

35

50

40 45 50	35	30	23	25	20	15	10	5	
			TABLE 3	e					
Composition (Weight I)	45:30:25	50:20:30	50:25:25	60:5:35	60:20:20	40:30:10 70:7.5:22.5	10:7.5:22.5	70:20:10 80:10:10	80:10:10
Critical Oxygen Index (I)	53	67	20	45	52	47	51	20	64
Toxicity Index Test	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Scrape Abrasion Test	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Flexure Endurance Test	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Low Temperature Test	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Resistance To Fluids Test									
Ethylene glycol	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Trichloroethane	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Isopropanol	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Phosphate Ester Based OX20	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Petroleum Based OM18	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
701/301 Isooctane/Toluene	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
DERV	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Synthetic OX38	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Deionised Water	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Sea Water	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Insulation Shrinkage Test	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Flammability Tests	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS

			100:2	FAIL	FAIL	PASS	PASS	PASS	FAIL	PASS	PASS	PASS	PASS
5			100:5	FAIL	FAIL	FAIL	PASS	PASS	FAIL	PASS	PASS	PASS	PASS
10			100:10	FAIL	FAIL	PASS	PASS	PASS	FAIL	PASS	PASS	PASS	PASS
			100:25	PASS	FAIL	FAIL	PASS	PASS	FAIL	PASS	PASS	PASS	PASS
15	1		100:50	PASS	FAIL	PASS	PASS	PASS	FAIL	PASS	PASS	PASS	PASS
20			100:100 100:50	PASS	FAIL	FAIL	PASS	PASS	FAIL	PASS	PASS	PASS	PASS
	S)		50:100	PASS	FAIL	PASS	FAIL	PASS	FAIL	PASS	PASS	PASS	PASS
25	TABLE		25:100	PASS	FAIL	PASS	PASS	PASS	FAIL		PASS	PASS	PASS
30			10:100	FAIL	FAIL	PASS	PASS	PASS	FAIL	PASS	PASS	PASS	PASS
			5:100	PASS	FAIL	PASS	FAIL	PASS	FAIL	PASS	PASS	PASS	PASS
35			2:100	PASS	FAIL	PASS	FAIL	PASS	FAIL	PASS	PASS	PASS	PASS
40		eight)					Based 0X20	OM18	ne/Toluene				
45		Composition (by weight)	Ultem:Siltem	Ethylene glycol	Trichloroethane	Isopropanol	Phosphate Ester Based OX20	Petroleum Based OM18	701/301 Isooctane/Toluene	>	Synthetic 0X38	Deionised Water	Sea Water
50		Сопро	Ultem	Eth	Tri	Iso	Pho	Pet	702	DERV	Syn	Dei	Sea

55 Claims

1. A blend comprising a poly(arylene ether ketone) together with a polyetherimide and a silicone-polyimide copolymer.

8. A blend according to any one of claims 1 to 7, wherein the polyetherimide contains units of the formula

10

5

in which Z and R are organic groups, R' is an alkyl, alkenyl, alkoxyalkyl, ketyl, ketenyl, fluoroalkyl or fluoroalkenyl group having at least 4 carbon atoms, or is a phenyl or substituted phenyl group, and R' is hydrogen or together with R' and the nitrogen forms an alicyclic group, obtainable by reacting a polyetherimide as specified in claim 7 with an amine of the formula R'-NH-R".

15

20

9. A blend according to any one of claims 1 to 8, wherein the polyetherimide contains units of the formula

25

in which Z and R are organic groups, R"'CO is an acyl or fluoroacyl group having at least 4 carbon atoms and X' is a halogen, obtained by reacting a polyetherimide as specified in claim 7 with an acyl or fluoroacyl halide of the formula R"'CO-X'.

30

10. A blend according to any one of claims 7 to 9, wherein Z is

45

or a group of the formula

$$-\bigcirc$$
 x^{d} $-\bigcirc$

50

in which X is C_vH_{2v},

enthält, in denen die Phenylengruppen einen oder mehrere Substituenten tragen können.

10 6. Blend nach Anspruch 3, wobei das Polyetherketonketon Wiederholungseinheiten der allgemeinen Formel

enthält, bei denen die Phenylengruppen einen oder mehrere Substituenten tragen können.

7. Blend nach einem der Ansprüche 1 bis 6, wobei das Polyetherimid Wiederholungseinheiten der allgemeinen Formel

enthält, in der Z und R organische Reste bedeuten.

35 8. Blend nach einem der Ansprüche 1 bis 7, wobei das Polyetherimid Einheiten der Formel

- enthält, in der Z und R organische Reste, R' einen Alkyl-Alkenyl-, Alkoxyalkyl-, Ketyl-, Ketenyl-, Fluoralkyl- oder Fluoralkenyl-Rest mit mindestens 4 Kohlenstoffatomen oder eine Phenyl- oder substituierte Phenylgruppe bedeutet und in der R' die Bedeutung von Wasserstoff hat oder zusammen mit R' und den Stickstoffatomen einen alicyclischen Rest bildet, erhältlich durch Umsetzen eines Polyetherimids wie in Anspruch 7 spezifiziert mit einem Amin der Formel R'-NH-R''.
 - 9. Blend nach einem der Ansprüche 1 bis 8, wobei das Polyetherimid Einheiten der Formel

50

5

20

25

30

10

5

enthält, in denen R₁ und R₂ organische Reste bedeuten.

- 13. Geformter Gegenstand, enthaltend ein Gemisch gemäß einem der Ansprüche 1 bis 12.
- 15 14. Geformter Gegenstand nach Anspruch 13 in Form einer Einfachschichtisolierung oder als innere und/oder äußere Schicht einer Doppelschichtisolierung, die für einen elektrischen Leiter angewandt wird.

Revendications

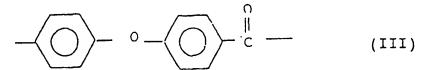
20

- Mélange comprenant une poly(arylèneéthercétone) avec un polyétherimide et un copolymère siliconepolyimide.
- 2. Mélange selon la revendication 1, dans lequel la poly(arylèneéthercétone) contient des unités de formules générales

30

qui peuvent porter un ou plusieurs substituants sur les cycles arylène.

- 35 3. Mélange selon la revendication 1 ou la revendication 2, dans lequel la poly(arylèneéthercétone) est une polyéthercétone, une polyéthercétone ou une polyéthercétone.
 - Mélange selon la revendication 3, dans lequel la polyéthercétone contient des unités constitutives de formule générale



45

40

dans laquelle les groupes phénylène peuvent porter un ou plusieurs substituants.

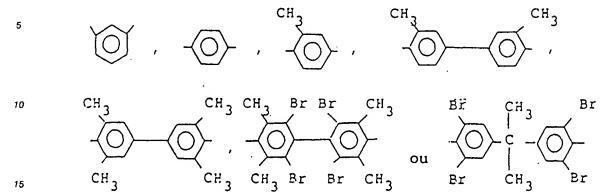
5. Mélange selon la revendication 3, dans lequel la polyétheréthercétone contient des unités constitutives de formule générale

55

dans laquelle les groupes phénylène peuvent porter un ou plusieurs substituants.

spécifié dans la revendication 7 avec un halogénure d'acyle ou de fluoroacyle de formule R'"CO-X'.

10. Mélange selon l'une quelconque des revendications 7 à 9, dans lequel Z est



ou un groupe de formule

dans laquelle X est CyH2y,

-O- ou -S-,

25

30

40

45

50

q est 0 ou 1 et y est un entier de 1 à 5, et les liaisons du groupe -O-Z-O- sont en position 3,3'; 3,4'; 4,3' ou 4,4'.

35 11. Mélange selon l'une quelconque des revendications 7 à 10, dans lequel R est

$$-$$
 ou $-$

12. Mélange selon l'une quelconque des revendications 1 à 11, dans lequel le copolymère siliconepolyimide contient des groupes de formule

$$R_1$$
-Si-O- et $-N$

où R₁ et R₂ sont des groupes organiques.

- 55 13. Article moulé comprenant un mélange selon l'une quelconque des revendications 1 à 12.
 - 14. Article moulé selon la revendidation 13, sous forme d'un isolant en couche simple ou sous forme de la couche interne et/ou externe d'un isolant à deux couches, appliqué sur un conducteur électrique.